Evaluating the variability of aquatic acidification and photochemical ozone formation characterization factors for Canadian emissions

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Abstract

Background, aim, and scope The Canadian life cycle impact assessment method LUCAS proposes a characterization of the impact categories aquatic acidification and photochemical ozone formation using a resolution scale based on 15 terrestrial ecozones. Each ecozone represents areas of the country which can be identified easily by general living (biotic) and nonliving (abiotic) characteristics. The three main purposes of this research are to improve the characterization models of both impact categories including regional exposure and effect factors, to investigate what is the best resolution scale between Canadian provinces or ecozones, and to analyze the extent of spatial variability.

Materials and methods A model framework accounting for variability in fate, exposure and effect factors has been elaborated. The same fate factor, based on Advanced Statistical Trajectory Regional Air Pollution matrices, applies to both impact categories. For the aquatic acidification impact category, the fate factor also accounts for the fraction of the deposition transferred to the aquatic ecosystem. The exposure factor for this impact category is considered to be 1 and the effect factor is based on the critical load exceedance, where the potential impacts are only considered in provinces or ecozones in which the critical load is exceeded. For the photochemical ozone formation impact category, the exposure factor is considered to be proportional to the population density in each province or ecozone, and the effect factor is represented by the chemical reactivity estimated with the maximum incremental reactivity model. The calculation of the new characterization factors using both a province-based and ecozone resolution scale was performed using a matrix which converts data from one resolution scale to another.

Results Results with the inclusion of the effect and the exposure factors show that the spatial variability between provinces remains within a factor of 10 and 5 for aquatic acidification and photochemical ozone formation, respectively.

Discussion Analysis of the results show that regionalization by province is preferable to regionalization by ecozone. It is more accurate in regard to atmospheric modeling and more representative of population distribution. However, averaging the fate factor and the population density over a whole province results in a serious limitation.

Conclusions The spatial variability of characterization factors between provinces is in the same order of magnitude as the overall range between chemicals for aquatic acidification while much smaller for photochemical ozone formation. Hence, at this stage of knowledge, province-based regionalization seems to be more relevant for the aquatic acidification impact category than for photochemical ozone formation.

Recommendations and perspectives Research must be pursued to integrate a better transport and deposition model with improved spatial capabilities and a successive modeling step properly describing the cause–effect chain up to the damage level, such as the biotic environment and the human population.

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Background, aim, and scope

For almost 20 years now, regional impacts such as aquatic acidification and photochemical ozone formation (POF) have been major environmental concerns in Canada. To address these issues, many initiatives and programs have been put forth which aim to reduce these impacts (Jeffries and Ouimet 2004). The inclusion of these two impact categories in the Canadian life cycle impact assessment (LCIA) method LUCAS (Toffoletto et al. 2006) is, therefore, justified. Aquatic acidification is caused by the emissions of nitrogen oxides (NO_x) and sulfur oxides (SO_2), while POF is caused by a photochemical reaction between NO_x and volatile organic carbons (VOC) in the atmosphere (Hertwich and Hammit 2001; Labouze et al. 2004). These pollutants can travel many thousands of kilometers, and, depending on the emission location, their overall effect on the environment can vary considerably. In LCIA, many research studies have already shown that the spatial differentiation and the resolution scale are important factors influencing the variability of the characterization factors (CFs). For example, the aquatic acidification CFs for Europe can vary up to 2 (Potting et al. 1998; Huijbregts et al. 2000; Seppälä et al. 2006) or 3.5 (Potting et al. 1998; Huijbregts et al. 2000; Seppälä et al. 2006) orders of magnitude depending on the emission location. For the US, the aquatic acidification CFs varies by a 0.5 order of magnitude compared to the national average (Bare et al. 2002). In all these models, the spatial variation depends on the transport and distribution processes, linking the emission location to the deposition of acidifying substances, the level of exposure to the pollutant, and the resulting potential effect on the ecosystem. The influence of spatial variability for POF on LCIA results was also considered important (from 2 to 4 orders of magnitude) in Europe as observed by Krewitt et al. (2001).

Two types of spatial resolutions are often used in LCIA: (1) based on political boundaries such as TRACI (Bare et al. 2002; Norris 2003), EDIP 2003 (Hauschild and Potting 2003), and CML (Guinée et al. 2001) and (2) based on regions with specific ecological and/or geological characteristics such as the ecozones used in LUCAS (Toffoletto et al. 2006) or watersheds used in IMPACT 2002+ (Jolliet et al. 2003; Pennington et al. 2005).

The European characterization models use atmospheric distribution and transport models with grid elements at a 50-km resolution scale such as RAINS or EMEP to calculate substance-specific source to receptor transfer matrices. The US method TRACI uses matrices produced by an atmospheric transport model named Advanced Statistical Trajectory Regional Air Pollution (ASTRAP). These matrices provide substance-specific source-to-deposition factors between the American states and Canadian provinces.

LUCAS (Toffoletto et al. 2006) is a midpoint impact assessment method that accounts for 15 terrestrial ecozones, each representing areas identified by their general living (biotic) and nonliving (abiotic) characteristics. An ecozone is an area where organisms and their physical environment endure as a system (Wiken 1986), thus, has no relation to watersheds. The characterization model for aquatic acidification, in addition to an atmospheric transport and deposition model (ASTRAP), accounts for the potential of the pollutant to migrate towards water using a so-called vulnerability factor. The effect is currently measured as the capacity of the substance to release protons, without taking into account the sensitivity of the destination area. For the POF impact category, CFs only integrate the transport of the pollutant and its relative reactivity using maximum incremental reactivity (MIR) values (Carter 1994). According to Hauschild and Potting (2003), this impact category should also include a human exposure modeling step to increase the environmental relevance since it covers more of the causality chain of human health.

To overcome part of the current limitations in the LUCAS LCIA model, this paper aims to: (1) develop site-dependent characterization factors for aquatic acidification and POF impact categories by considering Canadian-specific environmental regional characteristics; (2) identify the appropriate spatial resolution; and (3) analyze the extent of the spatial variability of fate, exposure, and effect factors, the latter factor being newly introduced in this paper.

Materials and methods

2.1 General framework

According to the general LCIA framework proposed by SETAC (Udo de Haes et al. 2002), the characterization factors—CFs (Impact/Mass)—for emission-related impact categories are expressed as the product of a fate factor (FF), an exposure factor (XF), and an effect factor (EF), as per Eq. 1:

$$[CF_{s,1}] = [FF_{s,d}] \times [XF_{d,x}] \times [EF_{x,1}] \qquad (1)$$

where the fate factor $[FF_{s,d}]$ (kg_d/kg_s) is a matrix representing the distribution of the pollutant in the destination compartments d per unitary emission in source compartment s. The exposure factor $[XF_{d,x}]$ (kg_x/kg_d) relates the chemical amount in destination compartment d to the exposed population x that represents the exposed ecosystem or human population of region d. The exposure factor is a square matrix (x has the same value as d in terms of number of lines and columns). Finally, the effect factor $EF_{x,1}$ (Impact/kg_x) stops at the midpoint (or problem along the cause–effect chain) level and represents the relative reactivity of the substance (i.e., capacity of the pollutant compared to the other contributing substances,

to form H+ ions in the case of acidification and O_3 in the case of POF) impacting the ecosystem or population.

2.2 Regionalized fate factor calculation

For the two impact categories, the fate factor, $[FF_{s,d}]$ (kg_d/kg_s) is given by the product of the source-to-deposition matrix $[D_{s,d}]$, the area of the destination regions A_d and an intermedia transfer factor f_d in regions d as per Eq. 2:

$$\left[FF_{s,d}\right] = \left[D_{s,d}\right] \times \left[A_{d,d}\right] \times \left[f_{d,d}\right] \qquad (2)$$

Where, $[D_{s,d}]$ ($kg_d/kg_s/km^2$) is the matrix of the annual weighted emission-to-deposition factor for a pollutant emitted in the source region s and deposited in region d, $[A_{d,d}]$ (km^2) is a diagonalized matrix of the areas for destination regions d, and $[f_{d,d}]$ (dimensionless) is a diagonalized matrix of the intermedia transfer fraction in the destination regions d, accounting for the characteristics of the media and the pollutants. Table 1 presents the matrices used in Eq. 2 to calculate the fate factor for aquatic acidification for Canadian provinces. The fate factor and emission–deposition matrix for photochemical ozone formation are presented in Appendix 1.

While several models exist for ozone formation in Canada (CHRONOS, AURAMS, and CMAQ), they are often too sophisticated to readily provide yearly average emission–deposition matrices for all Canadian provinces and American states for POF emissions (Gong et al. 2006; Pudykiewicz et al. 1997; Sirois et al. 1999; Smyth et al. 2006). ASTRAP is, to our current knowledge, the only atmospheric transport model providing (1) such matrices covering all the North American continent, (2) consistent results between acidification and photochemical ozone formation. Results of the ASTRAP model are aggregated by US states and by Canadian provinces. ASTRAP provides matrix distribution for SO_2 and NO_x for ten Canadian provinces, for 48 American states, and for the Great Lakes (for deposition only). Canadian territories and Alaska are not included. Outputs from ASTRAP were used to assess the fate of contributing substances for acidification and photochemical ozone formation with a similar calculation procedure as the one developed for TRACI. Since ASTRAP only provides the emission–deposition matrices for NO_x and SO_2, the fate of other pollutants was approximated based on these two matrices assuming similar regional transport as suggested by Norris (2003). This consists, for aquatic acidification, of using NO_x emission–deposition matrices for all the pollutants containing N, and SO_2 emission–deposition matrices for all other pollutants and, for POF, of using NO_x emission–deposition

matrices for VOCs. The fate factors are calculated for two types of Canadian regionalization scales: by province and by ecozone. Since ASTRAP matrices are only provided for a province resolution scale, they had to be modified to fit the ecozone resolution scale. A matrix composed of the shared area between provinces and ecozones was used for this purpose (Appendix 2). Fig. 1 shows the Canadian ecozones, provinces, and shared area.

As suggested by Toffoletto et al. (2006), for aquatic acidification, a vulnerability factor is introduced accounting for the capacity of the soil to diffuse pollution to groundwater (Meinardi et al. 1994; Klepper et al. 1995). The intermedia transfer fraction soil-to-surface water is therefore introduced under the assumption that all the pollutant transferred to groundwater is eventually transferred to surface water, i.e., $f_{d,d}$ being equal to the vulnerability factor. For POF, no intermedia transfer is needed, thus $f_{d,d}$ equals 1.

2.3 Regionalized exposure and effect factor calculations

2.3.1 Aquatic acidification

According to the German Federal Environmental Agency's (UBA 1996) definition, the critical load is a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge and under present conditions. The use of a sensitivity factor based on critical load to regionalize the effect of acidifying substances is common practice within LCIA (Huijbregts et al. 2000; Seppälä et al. 2006). It disregards the proportion of proton deposition that theoretically can be assimilated by the aquatic ecosystem. The proportion of harmful hydrogen ions exceeding the acidity critical load was used as a threshold as proposed by Huijbregts et al. (2000). The exposure and effect calculation were performed as shown in Eq. 3.

$$\left[XF_{d,x}\right] \times \left[EF_{x,1}\right] = \left[I_{d,x}\right] \times \left[CL_{x,1}\right] \times H^+ \qquad (3)$$

where $[XF_{d,x}]$ (kg_x/kg_d) is the exposure factor matrix, relating the chemical amount in the destination compartment d (surface water) with the exposed aquatic ecosystem x. It is assumed to be a unit matrix $[I_{d,x}]$, i.e., it is supposed that the aquatic ecosystem will be exposed to all the chemicals reaching the destination environment. $[EF_{x,1}]$ (mol H^+/kg_x) is a vector of the effect factor, quantifying the specific response to the pollutant exposure. It is expressed as the number of mol of H^+ released by kg of pollutant reaching the aquatic ecosystem. $[CL_{d,1}]$ (adimensional) is a

Table 1 Matrices used to calculate the fate factors for aquatic acidification

	Great Lakes	Alberta (AB)	British-Colombia (BC)	Manitoba (MB)	New-Brunswick (BR)	Newfoundland (NF)	Nova Scotia (NS)	Ontario (ON)	Prince Edward Island (PE)	Quebec (PQ)	Saskatchewan (SK)
$[FF_{s,d}]$ (kg_d/kg_s)											
AB	1.6E-02	2.0E-01	2.5E-02	8.0E-02	9.8E-04	5.5E-03	6.1E-04	5.8E-02	6.6E-05	4.0E-02	1.8E-01
BC	8.2E-03	1.5E-01	1.6E-01	3.6E-02	4.8E-04	2.7E-03	3.0E-04	2.8E-02	3.2E-05	2.0E-02	6.7E-02
MB	2.9E-02	1.9E-02	5.9E-03	2.1E-01	2.2E-03	1.2E-02	1.4E-03	1.3E-01	1.5E-04	9.0E-02	8.4E-02
BR	2.2E-03	7.9E-05	1.3E-05	9.5E-04	5.7E-02	6.4E-02	4.1E-02	7.5E-03	4.7E-03	1.1E-01	3.3E-04
NF	8.4E-04	5.7E-05	1.1E-05	6.2E-04	2.0E-03	1.7E-01	2.2E-03	3.6E-03	2.5E-04	4.5E-02	2.1E-04
NS	1.3E-03	4.9E-05	7.5E-06	6.0E-04	6.7E-03	6.6E-02	3.2E-02	4.7E-03	1.2E-03	4.5E-02	1.9E-04
ON	8.1E-02	4.2E-04	6.8E-05	5.1E-03	9.3E-03	2.9E-02	5.7E-03	1.7E-01	5.7E-04	2.3E-01	1.7E-03
PE	1.5E-03	5.8E-05	1.1E-05	6.9E-04	1.2E-02	6.7E-02	5.9E-02	5.3E-03	1.4E-02	5.9E-02	2.2E-04
PQ	1.7E-02	2.7E-04	4.6E-05	3.2E-03	1.6E-02	4.1E-02	8.6E-03	6.9E-02	1.0E-03	4.2E-01	1.1E-03
SK	3.2E-02	3.0E-02	7.9E-03	1.1E-01	1.6E-03	7.9E-03	1.0E-03	9.4E-02	1.1E-04	5.9E-02	1.6E-01
$[D_{s,d}]$ (kg_d/kg_s/km^2)											
AB	6.52E-08	4.69E-07	5.76E-08	1.83E-07	2.24E-08	1.72E-08	1.81E-08	8.36E-08	1.92E-08	3.47E-08	3.97E-07
BC	3.37E-08	3.67E-07	3.76E-07	8.31E-08	1.09E-08	8.40E-09	8.88E-09	4.07E-08	9.34E-09	1.70E-08	1.52E-07
MB	1.18E-07	4.60E-08	1.37E-08	4.78E-07	5.11E-08	3.88E-08	4.16E-08	1.91E-07	4.42E-08	7.74E-08	1.90E-07
BR	9.15E-09	1.89E-10	3.10E-11	2.19E-09	1.29E-06	2.00E-07	1.20E-06	1.08E-08	1.38E-06	9.09E-08	7.39E-10
NF	3.46E-09	1.37E-10	2.50E-11	1.43E-09	4.55E-08	5.18E-07	6.65E-08	5.11E-09	7.36E-08	3.89E-08	4.82E-10
NS	5.49E-09	1.17E-10	1.74E-11	1.39E-09	1.52E-07	2.07E-07	9.43E-07	6.71E-09	3.63E-07	3.85E-08	4.41E-10
ON	3.31E-07	1.01E-09	1.57E-10	1.18E-08	2.12E-07	9.02E-08	1.68E-07	2.38E-07	1.68E-07	1.98E-07	3.78E-09
PE	6.20E-09	1.39E-10	2.64E-11	1.59E-09	2.81E-07	2.08E-07	1.75E-06	7.56E-09	4.03E-06	5.08E-08	5.09E-10
PQ	6.93E-08	6.46E-10	1.07E-10	7.48E-09	3.71E-07	1.27E-07	2.53E-07	9.84E-08	2.92E-07	3.65E-07	2.40E-09
SK	1.29E-07	7.29E-08	1.83E-08	2.57E-07	3.71E-08	2.45E-08	3.00E-08	1.34E-07	3.10E-08	5.12E-08	3.56E-07
$[A_{d,d}]$ (km^2)											
Great Lakes	2.4E+05	0	0	0	0	0	0	0	0	0	0
AB	0	6.6E+05	0	0	0	0	0	0	0	0	0
BC	0	0	9.5E+05	0	0	0	0	0	0	0	0
MB	0	0	0	6.1E+05	0	0	0	0	0	0	0
BR	0	0	0	0	7.3E+04	0	0	0	0	0	0
NF	0	0	0	0	0	4.0E+05	0	0	0	0	0
NS	0	0	0	0	0	0	5.6E+04	0	0	0	0
ON	0	0	0	0	0	0	0	9.9E+05	0	0	0
PE	0	0	0	0	0	0	0	0	5.7E+03	0	0
PQ	0	0	0	0	0	0	0	0	0	1.5E+06	0
SK	0	0	0	0	0	0	0	0	0	0	6.4E+05
$[f_{d,d}]$ (dimensionless)											
Great Lakes	1.0E+00	0	0	0	0	0	0	0	0	0	0
AB	0	6.3E-01	0	0	0	0	0	0	0	0	0
BC	0	0	4.6E-01	0	0	0	0	0	0	0	0
MB	0	0	0	7.1E-01	0	0	0	0	0	0	0
BR	0	0	0	0	6.0E-01	0	0	0	0	0	0
NF	0	0	0	0	0	8.0E-01	0	0	0	0	0
NS	0	0	0	0	0	0	6.0E-01	0	0	0	0
ON	0	0	0	0	0	0	0	7.1E-01	0	0	0
PE	0	0	0	0	0	0	0	0	6.0E-01	0	0
PQ	0	0	0	0	0	0	0	0	0	7.7E-01	0
SK	0	0	0	0	0	0	0	0	0	0	6.9E-01

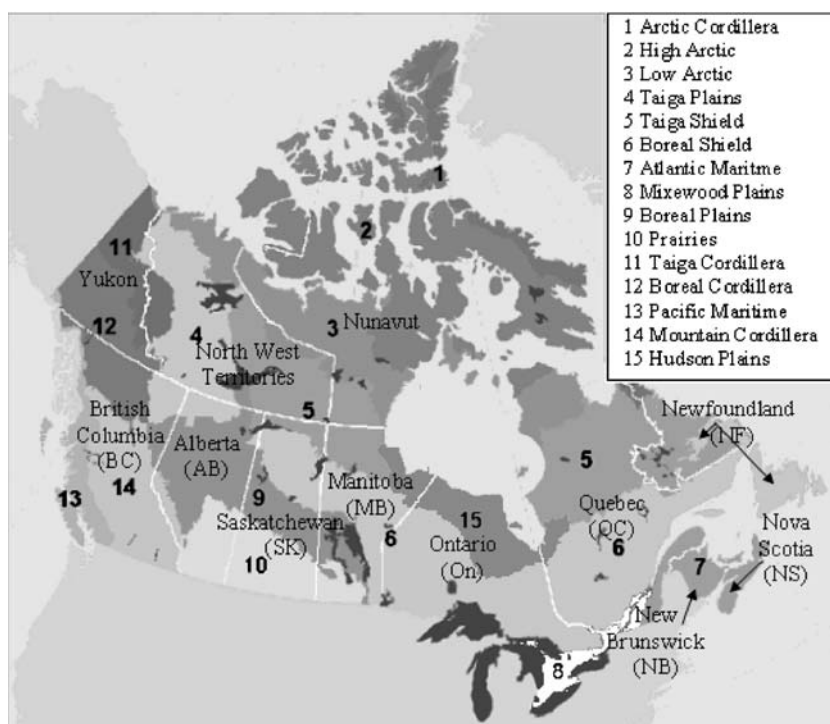$[FF_{s,d}]$, $[D_{s,d}]$ (Shannon, 1997), $[A_{d,d}]$ (Simard and Cameron 2002), and $[f_{d,d}]$

vector in which the elements are determined by a Heavy-side step function of the critical load exceedance of the destination compartment d: it equals 1 when the critical load is exceeded and 0 when not. H^+ (mol H^+/kg_x) is a scalar that represents the proportion of protons released per kilogram of pollutant as described by Norris (2003). The values of Canadian critical loads for aquatic acidification and their degree of exceedance were computed by Environment Canada using the model expert (Jeffries and Ouimet 2004) and SSWC (Henriksen and Posch 2001) under the assumption that a pH of 6 is an acceptable acidity level for the biota. The critical load

exceedance is only available for provinces, thus the exposure is only calculated for the province resolution scale. The potential capacity of soil and aquifer to neutralize the pollutant was not considered. Table 2 shows all the vectors used in Eq. 3 to calculate the exposure and effect factors for aquatic acidification (except for the unit matrix $I_{d,x}$).

2.3.2 Photochemical ozone formation

The photochemical ozone formation affects both the ecosystem and the human population. LUCAS currently

Fig. 1 Distribution of the Canadian provinces and ecozones through Canada, adapted from Natural Resources Canada (NRC 2006)

uses the MIR model (Carter 1994) to link pollutant concentration with ozone formation. The MIR model represents the maximum variation of ozone formation based on the variation of the concentration of reactive organic gas. It is used to compare the reactivity of the different VOCs in urban areas.

As an example, methane (which is not considered a great contributer to ozone formation) is less reactive than isobutene because MIR values for methane and isobutene are respectively of 0.15 and 1.21 g O_3/gVOC. This model was developed for North American urban areas and

provides values for a very large number of VOCs. Therefore, it is only adapted to model the cause–effect chain for the human population. The model is recommended by UNEP/SETAC Life Cycle Initiative (Udo de Haes et al. 2002) for poorly documented regions, which is the case for several Canadian provinces.

The EF is set as the MIR value of the substance for the moment because LUCAS is a midpoint method (the midpoint characterization in the cause effect chain is the formation of O_3) and does not evaluate damage to human health. Moreover, this choice is coherent with the future development of LUCAS to endpoint evaluation since the effect of ozone on humans does not vary in space.

An exposure factor was added to the POF impact category model of the first version of LUCAS (Toffoletto et al. 2006). Moreover, it was considered that there is no threshold exposure, that is, there is no concentration value at which no adverse effects on humans occur and which could be used as a critical level. The severity of the ozone health damage on human depends on the concentration and the duration of the exposure (McDonnell et al. 1983).

The exposure and effect factors are calculated according to Eq. 4:

Table 2 Vectors and data used to calculate the product of the exposure and the effect factor for aquatic acidification for sulfur dioxide (SO_2) emissions: $[XF_{d,x}]*[EF_{x,1}]$, $[CL_{d,x}]$, and H^+

	$[XF_{d,x}] \times [EF_{x,1}]$ (mol H^+/kg$_d$)	$[CL_{d,x}]$ (dimensionless)	H^+ (mol H^+/kg$_x$)
Great Lakes	62.3	1	62.3
AB	0	0	62.3
BC	0	0	62.3
MB	0	0	62.3
BR	62.3	1	62.3
NF	62.3	1	62.3
NS	62.3	1	62.3
ON	62.3	1	62.3
PE	0	0	62.3
PQ	62.3	1	62.3
SK	0	0	62.3

$$\left[XF_{d,x}\right] \times \left[EF_{x,1}\right] = \underbrace{\left[\frac{V_{\text{inh}}}{H^{\text{mix}}}\right] \times \left[\left(\frac{P}{A}\right)_{d,x}\right]}_{XF} \times \underbrace{MIR \times \left[e_{x,1}\right]}_{EF}$$

(4)

where $[XF_{d,x}]$ (kg_x/kg_d/year) is the vector of the exposure factors, relating the chemical amount in the destination compartment r with the amount x exposing the human population every year in compartment d (or province). $[V_{inh}/H^{mix}]$ is a scalar representing the ratio between the volume of air annually inhaled by a person, V_{inh} (7,300 m^3/year/person), and the mixing height used to approximate the potential concentration of pollutant near the soil level in urban areas, H^{mix} (400 m from (Environment Canada 2005)). $[P_x/A_d]$ (person/m^2) is the population density matrix whose diagonal elements are the ratio between population P_x and Area A_d of each Canadian province (d). As the average mixing height and the inhalation rate are constant terms, the exposure factor for the same substance varies between different regions according to the population density alone. $[EF_{x,1}]$ (moles of O$_3$/kg$_x$) is a vector of the effect factor, quantifying the relative amount of photochemical ozone formed to which the population is exposed. It is expressed as moles of O$_3$ to which the population is exposed per kilogram of pollutant. MIR is a scalar value representing the maximum incremental reactivity of the substance (moles of O$_3$ formed/kg VOC). $[e_{x,1}]$ is a vector of ones (1) used for mathematical purposes. The combination of the exposure factor with fate factor in Eq. 2, results in a potential "intake fraction" of ozone. Table 3 shows all the vectors used in Eq. 4 to calculate the exposure and effect factors for photochemical ozone formation (except for the unit vector $[e_{x,1}]$).

Results and discussion

3.1 Fate factor calculation

Figures 2 and 3 show respectively provinces, and ecozones (initial LUCAS differentiation) atmospheric deposition of nitrogen oxide for an emission from four different prov-

inces and ecozones across Canada. Two observations can be made: (1) The deposition of pollutants is generally higher in regions where the pollutant is emitted and (2) the pollutants emitted in the atmosphere generally travel with the West–East Canadian prevailing winds (Fisher et al. 2002).

Important differences are to be observed between Figs. 2 and 3. Particularly, Fig. 3c and d show that the NO$_x$ deposition does not follow the Canadian West–East prevailing winds as in Fig. 2, where provinces are used as spatial resolution. This is caused by a model artifact created when interpolating fate factors from province to ecozone resolution. This interpolation has the effect of artificially averaging and diluting the original fate factors by province, mainly disposed in the North–South direction into ecozones disposed in a West–East direction. This is observed particularly for Northern Arctic (one), Atlantic Maritimes (seven) and Hudson Plains (15) ecozones. Furthermore, the characterization factors of Nordic ecozones (Arctic Cordillera (one), Northern Arctic (two), Southern Arctic (three), Taiga Plains (four), Taiga Cordillera (11), and Boreal Cordillera (12)) are not representative because a significant portion of their areas are located in the Canadian territories which are not integrated in the atmospheric model ASTRAP. As an example, the area of ecozone 2 which is integrated in the ASTRAP model represents only 2% of the total area of the ecozone (Simard and Cameron 2002). Defending the relevance of ecozone boundaries in the context of atmospheric modeling is therefore problematic and will no longer be used in this paper. The same phenomenon was observed by Pennington et al. when attempting to transform an air grid atmospheric model into watershed delimitations (Pennington et al. 2005). For aquatic acidification, the fate factor also includes the fraction of the atmospheric deposition that is deposited on surface water and that is transferred from soil to fresh water, f_r.

Table 3 Vectors and data used to calculate the product of the exposure and the effect factor for photochemical POF for ethylene (C$_2$H$_4$) emissions

	$[XF_{d,x}] \times [EF_{x,1}]$ (kg O$_3$/kg$_d$)	T_{inh}/H_{mix} (m^2/year/inh)	$[(P/A)_{d,x}]$ (inh/km^2)	T_{inh}/H_{mix} (m^2/year/inh)	MIR (kg O$_3$/kg$_d$)
AB	13.30	18.25	4.96	18.25	14.68
BC	12.04	18.25	4.49	18.25	14.68
MB	5.18	18.25	1.93	18.25	14.68
BR	27.48	18.25	10.25	18.25	14.68
NF	3.45	18.25	1.29	18.25	14.68
NS	44.61	18.25	16.65	18.25	14.68
ON	34.10	18.25	12.73	18.25	14.68
PE	64.88	18.25	24.21	18.25	14.68
PQ	13.52	18.25	5.04	18.25	14.68
SK	4.15	18.25	1.55	18.25	14.68

$[XF_{d,x}]*[EF_{x,1}]$, $[(P/A)_{d,x}]$ (Simard and Cameron 2002, Statistics Canada 2005), T_{inh}/H_{mix} (Horwat and Meyer 1998, Environment Canada 2005), and MIR (Carter 1998)

Fig. 2 Provincial atmospheric deposition ($D_{s,d}$) of nitrogen for an emission of 1 kg of nitrogen oxides in the provinces (*shown by the arrow*) of **a** British-Colombia, **b** Manitoba, **c** Quebec, and **d** Newfoundland
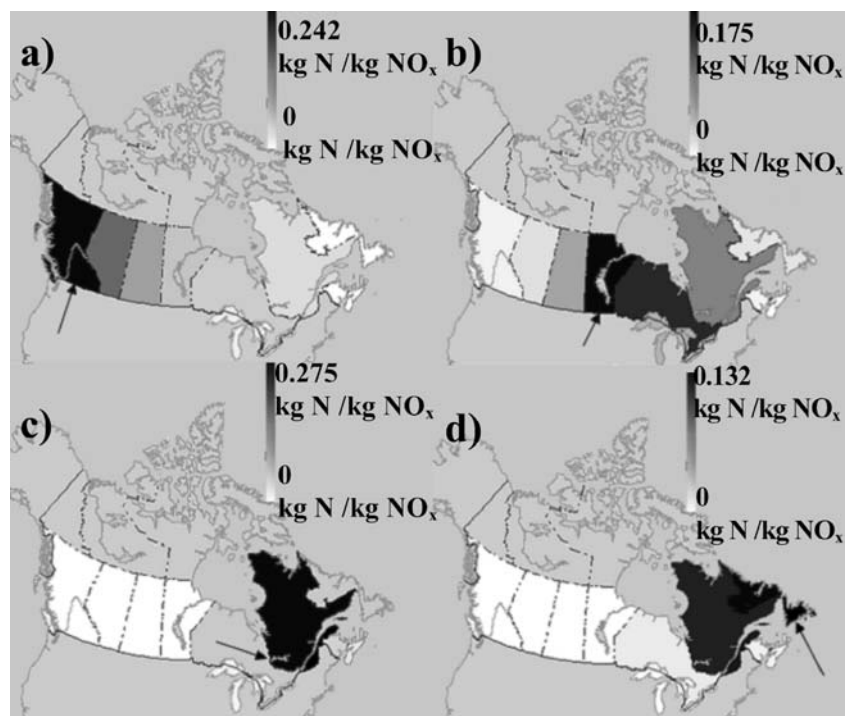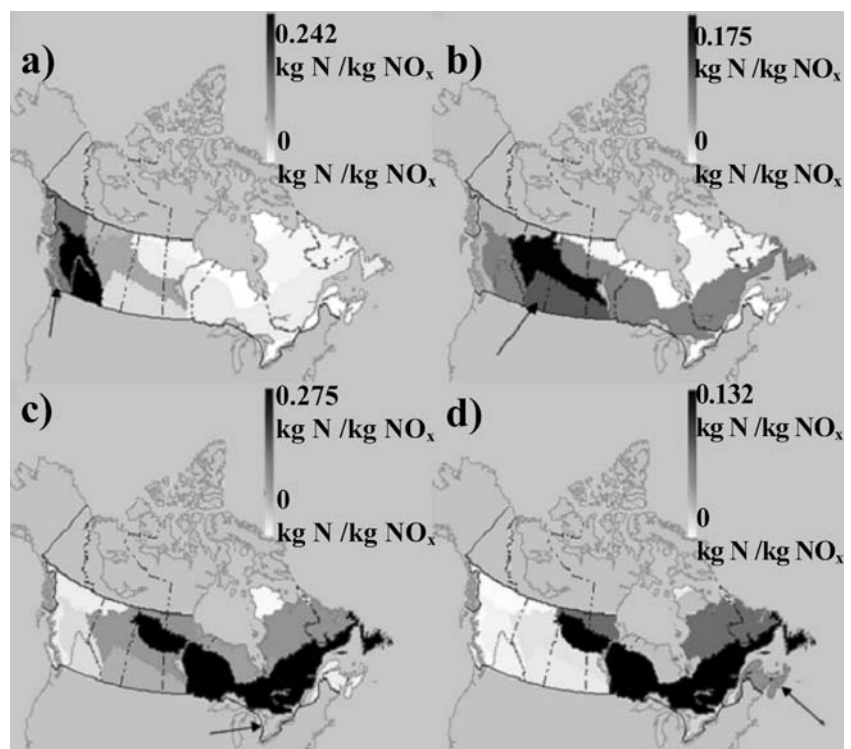

Fig. 3 Ecozone atmospheric deposition ($D_{s,d}$) of nitrogen for an emission of 1 kg of nitrogen oxide in the ecozones (*shown by the arrow*) of **a** Pacific Maritimes, **b** Prairies, **c** Mixed Wood plains, and **d** Atlantic Maritimes

3.2 Combined fate, exposure, and effect factor determination

3.2.1 Aquatic acidification

Figure 4 compares the final SO_2 CFs for aquatic acidification calculated as currently done in LUCAS method (original CFs), i.e., with a constant effect factor over all Canadian provinces (histogram in black) versus the updated CFs with the effect factor varying between different regions (dashed histogram). The comparison between the dashed and the black histograms in Fig. 4 determines the importance of introducing a regionalized effect factor. Results are presented for nine provinces from Western (left) to Eastern (right) Canada. The variability of the original CFs (with a constant effect factor) depends on the fate factor only. The fate factor is higher for emissions taking place in the Western provinces (on the left side of Fig. 4), because the pollutants are transported and deposited East on other provinces following the prevailing winds. Overall, the original CFs of acidifying substances are proportional to the effect factor since they are all based on the fate factor of SO_2 or NO_x (for substances containing N). Figure 4 only shows results for SO_2. Similar results are observed for substances containing N and having a NO_x-based fate factor. The closer the emission to the Atlantic Ocean, the higher the losses over the ocean and therefore the smaller the fate factor.

The highest updated CFs with regionalized effect are observed for emissions taking place in Ontario (ON) and Québec (QC) and become lower when moving from East to West for two different reasons: (1) from British Columbia

(BC) to Manitoba (MB), despite a higher fate factor, the final CF result diminishes because in several western provinces, the critical load is not exceeded (see CL factors in Eq. 3). The effect factor influences the variability of the CFs from a factor of 2 (MB) to a factor of 10 (BC). (2) From Ontario to the eastern provinces, the critical load is exceeded almost everywhere. The characterization factors for these provinces, thus, are directly proportional to their fate factor.

For all the characterized substances obtained, updated CFs using the regionalized effect factor tend to be lower in western provinces compared to the national average because most of the emitted pollutant will deposit in provinces where the critical loads are not exceeded. Only the aquatic critical load exceedance was considered. The buffer potential of soil or underground water was not included in the calculations. This implies that the CFs results are possibly overestimated. This overestimation, however, is minimal since according to Jeffries and Ouimet (2004), terrestrial and aquatic critical load exceedances touch the same regions of Canada. It would be interesting to use a long-term critical load to take into account the long-term change in the critical load as proposed by Huijbregts et al. (2000). To calculate the long-term critical load, it would have been necessary to use a fate model that would consider the overall emissions of North America and to calculate the level of deposition in each destination environment which was not available. Huijbregts et al. (2000) considered in their model both the exceedance of the critical load and the rate at which the critical load fills up. To do so, they used a dose-response function inversely proportional to the critical load.

The inclusion of an effect factor accounting only for the area exceeding the critical load can reduce the magnitude of the characterization factors up to 80% when assessing regional emissions in Canada. This concurs with results obtained in Europe (Huijbregts et al. 2000; Guinée et al. 2001) for which reductions of up to 95% where observed.

The Canadian generic CFs, or national averages, for regionalized fate and effect can be calculated in two ways: by averaging the nine CFs of each province (so-called multibox model in Fig. 4) and by multiplying averaged fate and averaged effect factors over Canada (so-called single-box model in Fig. 4), the difference between the results being a factor of 1.55 in the case of SO_2 emissions. In this paper, the multibox average is used because the authors believe that calculating the CFs for each province better reflects reality. The national averages, for example, are 20.4 and 32.2 H^+ equivalents for the NO_x and the SO_2 (or 0.68 and 1 SO_2 equivalent), respectively.

The variability of the CFs among the provinces compared to the national average gives an indication on the uncertainty of the generic characterization factor. The range in this paper is between 20% and 180% of the national average, which compares well with the results for US method
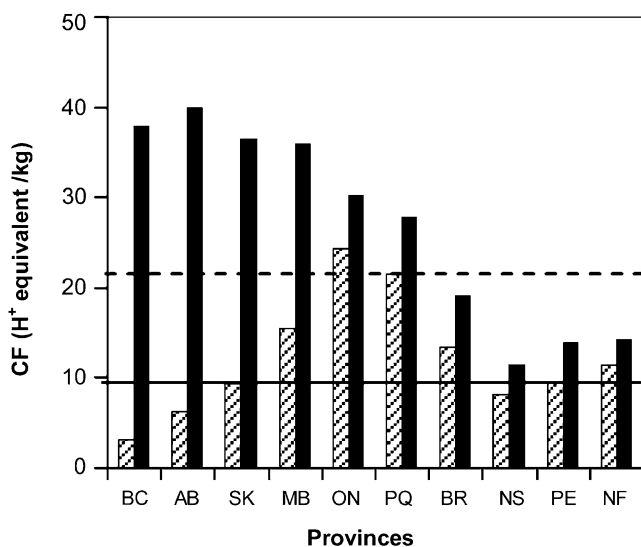

Fig. 4 Variation of the original CFs with a constant effect factor (*black histogram*) versus the updated CFs with regionalization of the effect factor (*dashed histogram*) for sulfur dioxide (SO_2) emissions for the aquatic acidification impact category. The *dotted line* is for the national average multibox and *plain line* for the national average single-box

TRACI (Norris 2003): between 20% and 160%. In the case of European methodologies, this variation is larger: from 10% to 400% of the national average for Heijungs et al. (1992), from 1% to 740% for Huijbregts et al. (2000), and from 2% to 620% for Seppälä et al (2006). The restricted spatial variability observed in Canada and in the US could be explained by the lower resolution of the fate model, compared to the ones used in Europe: ASTRAP provides results at the county and province level while the RAINS model provides results using a 50-km resolution grid.

Furthermore, the variability in CF values introduced by regionalizing the effect factor (0.6 orders of magnitude) is about the same as the variability observed between the CF of all the characterized substances (0.56 orders of magnitude). The maximum, the minimum and the standard deviation of characterization factors between substances are respectively 80 mol H^+ equivalents/kg, 14 mol H^+ equivalents/kg and 19 H^+ mol equivalents/kg. This situation shows that the regionalization of the effect factor is as important as the differentiation of substances.

3.2.2 Photochemical ozone formation

Figure 5 shows the variation of the ethylene CFs for the nine provinces of Canada. As mentioned above, all the VOCs use the same fate factor based on NO_x. The variation of CF is therefore influenced by the regional variation of the exposure factor and effect factor, specific to each substance (see Eq. 4). The dark histogram represents the CFs calculated as in the current version of LUCAS, i.e. with a fate factor based on NO_x, a constant exposure factor, i.e. equal to 1, and a substance-specific effect factor provided by MIR. CFs are higher for emissions taking place in the Western

provinces (on the left side of Fig. 5), because of the West–East prevailing winds. The dashed histograms represent CFs including regionalized exposure factors, but with the same fate and effect factor as in the dark histograms. The highest CF is associated with emissions taking place in Ontario, because of a relatively high fate factor and a high exposure factor, this latter driven by the higher population density in this province and along the corridor going from the Great Lakes through the St. Lawrence River. The CFs for the Atlantic provinces tend to decrease, because of a lower fate factor in spite of their higher population densities.

The generic CFs are 1 and 1.02 kg-ethylene eq./kg for the multibox model and the single-box model, respectively. The spatial variability between CFs along the different provinces range from 25% to 120% when compared to the generic CF for the single-box model. This range is comparable to the one found using TRACI, which ranges from 20% to 150% of the US average (Norris 2003). The exposure factor contributes to the overall variability of the CFs up to 73%. Canada has a population density of 3.3 pers/km² compared to 31 pers/km² for the US and 118 pers/km² for the European Union (CIA 2004). The population densities can vary from less than 1 pers/km² in the countryside to more than 20,000 pers/km² in the big cities. Since the MIR is representative for conditions observed in urban areas (Carter 1998), future work should focus on the use of a transport and deposition model with a higher resolution grid to target such highly populated urban areas. Averaging the fate factor and the population density over a whole province results in a serious limitation. The CFs between all the photochemical ozone formation substances are included in a range of 4 orders of magnitude compared to a range of 0.5 orders of magnitude for the CFs between regions. The maximum, the minimum, and the standard deviation of CFs between substances are, respectively, 2.27, 0.0001, and 0.4 moles O_3/kg. This situation shows that the regionalization of the effect factor is restricted compared to the differentiation between the different substances, i.e., efforts to reduce LCIA results uncertainty should focus on substance differentiation and not necessarily on effect regionalization.

Conclusions

This paper generated improved characterization factors for aquatic acidification and photochemical ozone formation to assess the environmental impact of Canadian life cycle inventories and analyze their variability for two regionalization scales. Our observations definitely discarded the choice of using ecozones as a basis for the regionalization and favored, at this stage of knowledge, the regionalization by provinces; this latter being more accurate in relation to the atmospheric modeling and more representative for

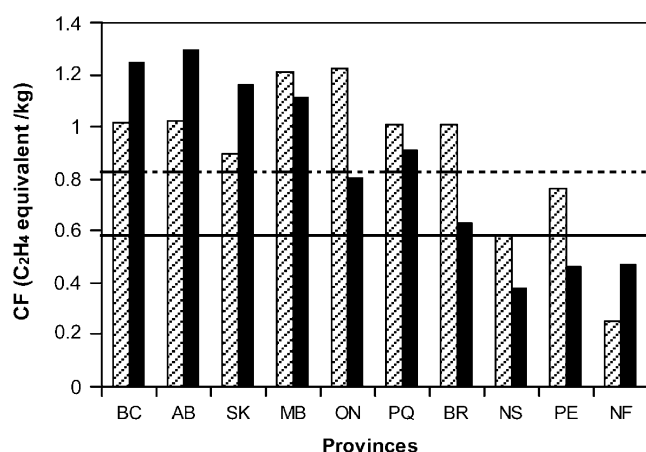Fig. 5 Variation of the CFs for POF with constant exposition factor equal to 1 (*black histogram*) versus CFs with regionalization of exposition factor (*dashed histogram*) for ethylene expressed in kilogram ethylene (C_2H_4) equivalents. The equivalency was calculated using the ethylene generic CF. The *dotted line* is for the national average multibox and *plain line* for the national average single-box

population distribution. The variability of the CFs between provinces provides a first estimation of the uncertainty when using a generic CF. We found that it ranges between a factor of 10 and 5 for aquatic acidification and POF, respectively. This spatial variability is in the same range as the variation between the pollutants for aquatic acidification (factor of 9) but much smaller than the variation between pollutants in the case of photochemical ozone formation (factor of 5 in comparison with 4 orders of magnitude).

Recommendations and perspectives

The inclusion of an effect factor based on the critical load exceedance enabled us to further discriminate the characterization factors for aquatic acidification (up to a factor of 10). The introduction of the exposure factor for POF resulted in a less significant variation, because of the modeling resolution capability of the fate model that was too low, implying the need of averaging the population densities over the whole province when we know that more than 90% of the Canadian population lives within a 500-km band north of the US border.

To improve this situation, the use of an atmospheric pollutant transport and deposition model with higher resolution, like the European RAINS model (Labouze et al.

2004), is required to better discriminate between urban and rural areas and eventually between sensitive and nonsensitive areas. In addition, to overcome the current limitation of not considering the full extent a chemical's distribution in the environment, the new model should also include the transport and the deposition of pollutants over the US. The assumption of VOC behaving in the same way as NO_x should also be validated when data will be available.

Temporal differentiation should also be considered. The annual averaging of the VOC emission, given the volatility of the ozone concentration in the course of a day and between seasons, is also a serious limitation of the model which should be addressed in the choice of a new transport and deposition model.

Finally, both aquatic acidification and photochemical ozone formation impact categories are presently modeled in LUCAS as midpoint impact categories and do not account for a successive modeling steps to the damage level such as the biotic environment and the human population. The inclusion of an exposure factor is a first step in this direction for POF, which should be pursued with a human dose-response assessment step. Similarly, for aquatic acidification, one should link the reactivity of the chemical in the destination environment with an indicator at the damage level related to the loss of biodiversity as suggested by Zelm and Huijbregts (2006).

Appendix 1

Table 4 Matrices used to calculate the fate factors for POF: [FF$_{s,d}$] and [D$_{s,d}$] (Shannon 1997)

	Great Lakes	Alberta (AB)	British-Colombia (BC)	Manitoba (MB)	New-Brunswick (BR)	Newfoundland (NF)	Nova Scotia (NS)	Ontario (ON)	Prince Edward Island (PE)	Quebec (PQ)	Saskatchewan (SK)
[FF$_{s,d}$] (kg$_d$ /kg$_s$)											
AB	6.5E-03	1.1E-03	2.3E-03	3.5E-05	1.4E-04	2.1E-05	1.9E-03	2.3E-06	1.1E-03	4.9E-03	6.5E-03
BC	4.6E-03	8.0E-03	1.1E-03	1.8E-05	7.6E-05	1.1E-05	9.0E-04	1.2E-06	5.9E-04	2.0E-03	4.6E-03
MB	3.5E-04	1.3E-04	5.7E-03	8.2E-05	3.0E-04	5.0E-05	5.1E-03	5.3E-06	2.4E-03	1.3E-03	3.5E-04
BR	1.9E-06	3.4E-07	2.5E-05	2.2E-03	1.5E-03	2.0E-03	2.3E-04	1.7E-04	2.6E-03	7.9E-06	1.9E-06
NF	1.7E-06	4.2E-07	2.1E-05	9.2E-05	4.3E-03	9.6E-05	1.3E-04	1.1E-05	1.8E-03	6.6E-06	1.7E-06
NS	1.1E-06	1.8E-07	1.6E-05	3.7E-04	1.5E-03	1.8E-03	1.5E-04	6.1E-05	1.3E-03	4.6E-06	1.1E-06
ON	9.6E-06	2.0E-06	1.3E-04	3.2E-04	6.4E-04	2.0E-04	4.8E-03	1.9E-05	5.0E-03	3.9E-05	9.6E-06
PE	1.3E-06	2.6E-07	1.9E-05	4.7E-04	1.7E-03	1.8E-03	1.7E-04	4.4E-04	1.7E-03	5.7E-06	1.3E-06
PQ	4.1E-06	8.4E-07	4.9E-05	8.7E-04	1.1E-03	4.2E-04	1.1E-03	4.4E-05	9.0E-03	1.6E-05	4.1E-06
SK	1.1E-03	3.6E-04	3.5E-03	5.5E-05	2.1E-04	3.3E-05	2.8E-03	3.6E-06	1.7E-03	6.4E-03	1.1E-03
[D$_{s,d}$] (kg$_d$/kg$_s$/km^2)											
AB	4.87E-08	3.00E-07	3.58E-08	1.13E-07	1.47E-08	1.09E-08	1.16E-08	5.71E-08	1.22E-08	2.29E-08	2.32E-07
BC	2.37E-08	2.13E-07	2.55E-07	5.38E-08	7.56E-09	5.78E-09	6.15E-09	2.78E-08	6.46E-09	1.18E-08	9.35E-08
MB	1.32E-07	1.61E-08	4.18E-09	2.87E-07	3.42E-08	2.27E-08	2.69E-08	1.55E-07	2.81E-08	4.88E-08	6.31E-08
BR	6.17E-09	8.84E-11	1.10E-11	1.23E-09	9.33E-07	1.15E-07	1.07E-06	7.04E-09	9.22E-07	5.18E-08	3.77E-10
NF	2.65E-09	7.99E-11	1.35E-11	1.03E-09	3.83E-08	3.30E-07	5.19E-08	4.05E-09	6.04E-08	3.71E-08	3.14E-10
NS	3.95E-09	5.11E-11	5.64E-12	7.83E-10	1.54E-07	1.17E-07	9.53E-07	4.56E-09	3.27E-07	2.63E-08	2.20E-10
ON	3.36E-07	4.42E-10	6.25E-11	6.32E-09	1.34E-07	4.86E-08	1.07E-07	1.49E-07	1.03E-07	1.01E-07	1.83E-09
PE	4.35E-09	6.18E-11	8.26E-12	9.48E-10	1.93E-07	1.33E-07	9.94E-07	5.18E-09	2.35E-06	3.43E-08	2.68E-10
PQ	1.82E-08	1.90E-10	2.70E-11	2.46E-09	3.61E-07	8.31E-08	2.29E-07	3.45E-08	2.34E-07	1.82E-07	7.61E-10
SK	8.11E-08	5.18E-08	1.15E-08	1.75E-07	2.27E-08	1.57E-08	1.81E-08	8.69E-08	1.89E-08	3.35E-08	3.01E-07

Appendix 2

Table 5 Transfer matrices

	AB (%)	BC (%)	MB (%)	BR (%)	NF (%)	NS (%)	ON (%)	PE (%)	PQ (%)	SK (%)
1	0	0	0	0	51	0	0	0	49	0
2	0	0	4	0	0	0	0	0	96	0
3	0	0	0	0	0	0	0	0	100	0
4	48	52	0	0	0	0	0	0	0	0
5	1	0	14	0	24	0	0	0	56	5
6	0	0	13	0	8	0	34	0	35	10
7	0	0	0	36	0	27	0	3	34	0
8	0	0	0	0	0	0	85	0	15	0
9	53	5	17	0	0	0	0	0	0	25
10	33	0	15	0	0	0	0	0	0	52
11	0	0	0	0	0	0	0	0	0	0
12	0	100	0	0	0	0	0	0	0	0
13	0	100	0	0	0	0	0	0	0	0
14	10	90	0	0	0	0	0	0	0	0
15	0	0	20	0	0	0	70	0	11	0

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